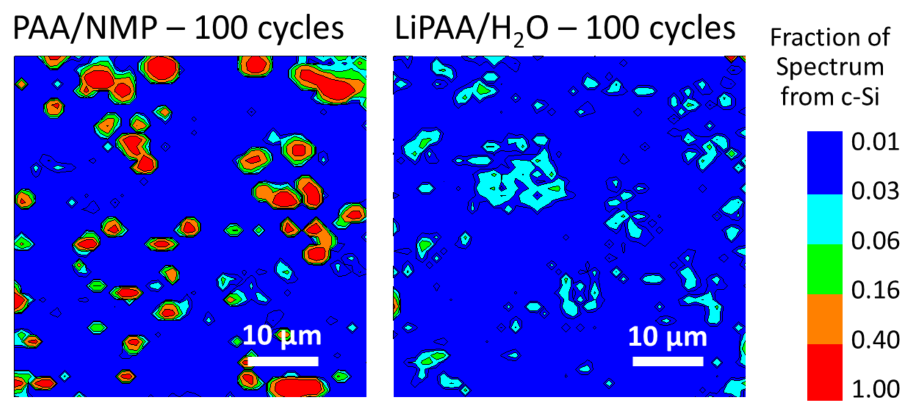
NEXT GENERATION ANODES FOR LITHIUM-ION BATTERIES: ELECTRODE CHARACTERIZATION AND ANALYSIS

Silicon Deep Dive



STEVE TRASK

DANIEL ABRAHAM

U.S. DEPARTMENT OF ENERGY
VEHICLE TECHNOLOGIES OFFICE
2018 ANNUAL MERIT REVIEW

Project ID BAT350

This presentation does not contain any proprietary, confidential, or otherwise restricted information

OVERVIEW

Timeline

- Start: October 1, 2015
  - Reset: October 1, 2017
- End: September 30, 2020
- Percent Complete: 55%

Budget

- Total project funding:
  - FY18 - $3600K
- Presentations: BAT349, BAT350, BAT351, BAT352, and BAT353

Barriers

- Development of PHEV and EV batteries that meet or exceed DOE and USABC goals
  - Cost, Performance, and Safety

Partners

- Sandia National Laboratories
- Pacific Northwest National Laboratory
- Oak Ridge National Laboratory
- National Renewable Energy Laboratory
- Lawrence Berkeley National Laboratory
- Argonne National Laboratory

RELEVANCE

- **Objectives: Stabilize the SEI - Stabilize the electrode**
- **Overall focus on insights into and advancement of silicon-based materials, electrodes, and cells.**
- **Advancements verified on life and performance of full cells using standardized testing protocols.**

Program Directly Addresses Cost and Performance Barriers and Quantifies Safety

- Elemental silicon can theoretically store >3500 mAh/g.
- Battery Performance and Cost (BatPaC) Model indicates a silicon based anode coupled with a high capacity cathode lithium-ion technology presents a pathway to less than $125/kWh$_{use}$
- BatPaC also used to relate pack level benefits to program goals.
- Benefits reach diminishing returns after **1000 mAh/cm^3** (electrode basis) for both cost and energy density.
- Silicon with <75 wt% graphite can achieve target.

MILESTONES AND ACTIVITIES

- **The program has more than twenty milestones related to the broad range of integrated activities listed below.**
- **Generally, milestones are either completed or on schedule.**

- Extensive electrochemical and analytical diagnostic studies.
- Facilities supporting program through a wide range of studies.
  - Battery Abuse Testing Laboratory (BATLab); Battery Manufacturing Facility (BMF); Cell Analysis, Modeling, and Prototyping (CAMP) Facility; Materials Engineering Research Facility (MERF); Post-Test Facility (PTF)
- Development and testing of coatings and additives designed to modify and stabilize the interface.
- Develop and analyze polymer binders designed to accommodate volume changes, increase conductivity, and improve adherence.
- Active material development.
  - Explore lithium inventory strategies.
  - Study alternative high-energy metals.

For reviewers, a detailed list of the milestones and progress is supplied in the reviewers only slides.

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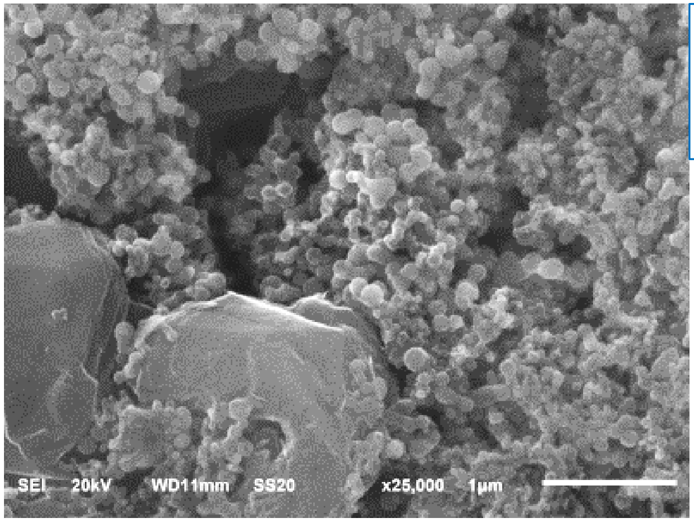
APPROACH

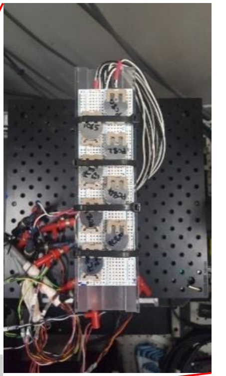
- Si and Graphite are both electrochemically active in the Si-Gr electrodes
  - Operando Energy Dispersive X-ray Diffraction (EDXRD) was conducted to determine relative lithiation/delithiation behavior of the Si and Gr components.
- Calendar-life aging conditions are common in practical applications, for example when an automotive battery is left in a fully charged state and not in use
  - Electrochemical experiments were conducted to compare cell performance during cycle life and calendar aging conditions. NMC532/Si-Gr cells were either cycled between 3-4.1 V or held at 4.1 V for a comparable time period.
- Electrochemical activity of Si-Gr electrodes is impacted by processing parameters
  - Raman micro-spectroscopy can distinguish between intrinsic factors that limit performance (volume expansion, SEI instability) from extrinsic factors that can be improved with processing (electrode heterogeneity, incomplete lithiation).
- Silicon content in electrodes increases gas/heat generation during abuse conditions. How does abuse response correlate with material/electrode properties?
  - Conduct electrochemical formation and cycling experiments followed by calorimetry (ARC and DSC) to evaluate various material property contributions to runaway enthalpy.
- Aqueous processing of Si-Gr electrodes can lead to gas (H_2) generation
  - A method, based on the Archimedes principle, was developed to quantify the volume of gases generated by reactions of Si with the slurry components.

Si AND GRAPHITE ARE BOTH ELECTROCHEMICALLY ACTIVE IN Si/GR ELECTRODES

Electrochemical activity of the components can be studied using operando Energy Dispersive X-ray Diffraction (EDXRD)

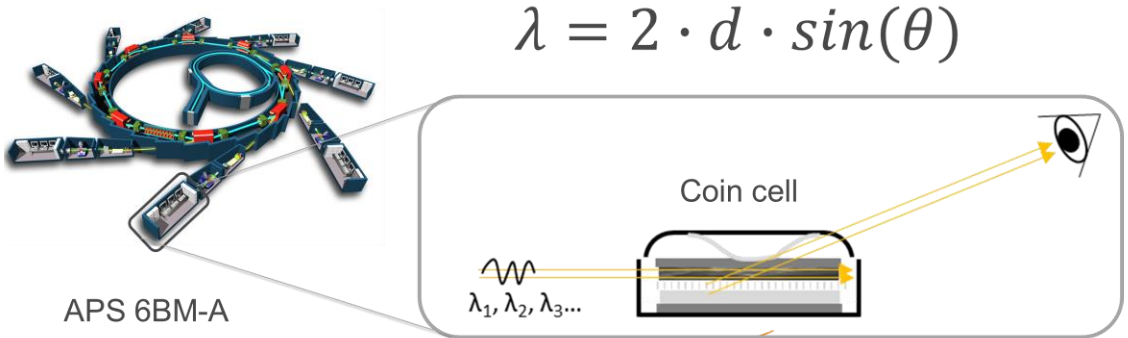


SEM micrograph showing electrode with 15 wt% Si (NanoAmor, 50-70 nm) & 73 wt% graphite (Mag-E)



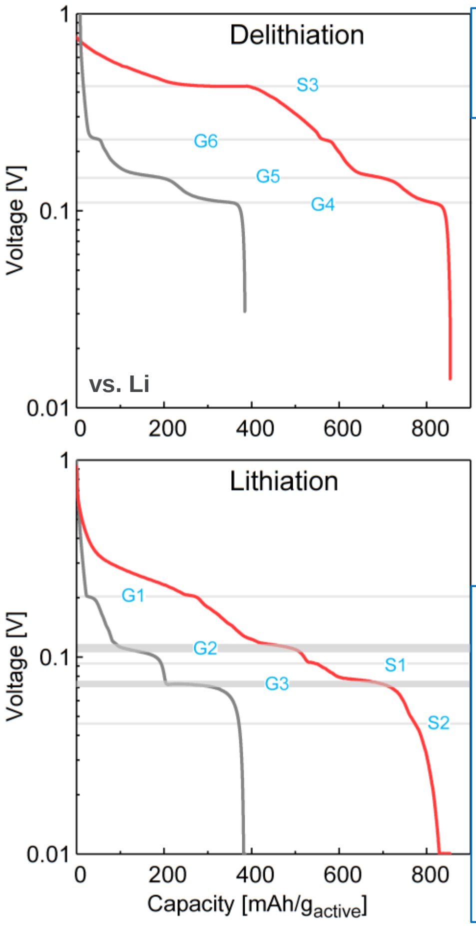
Multiple coin cells can be monitored simultaneously

$$\lambda = 2 \cdot d \cdot sin(\theta)$$



CHARACTERIZATION OF GR AND Si/GR (15/73 w/w) ELECTRODES (AFTER FORMATION CYCLES)

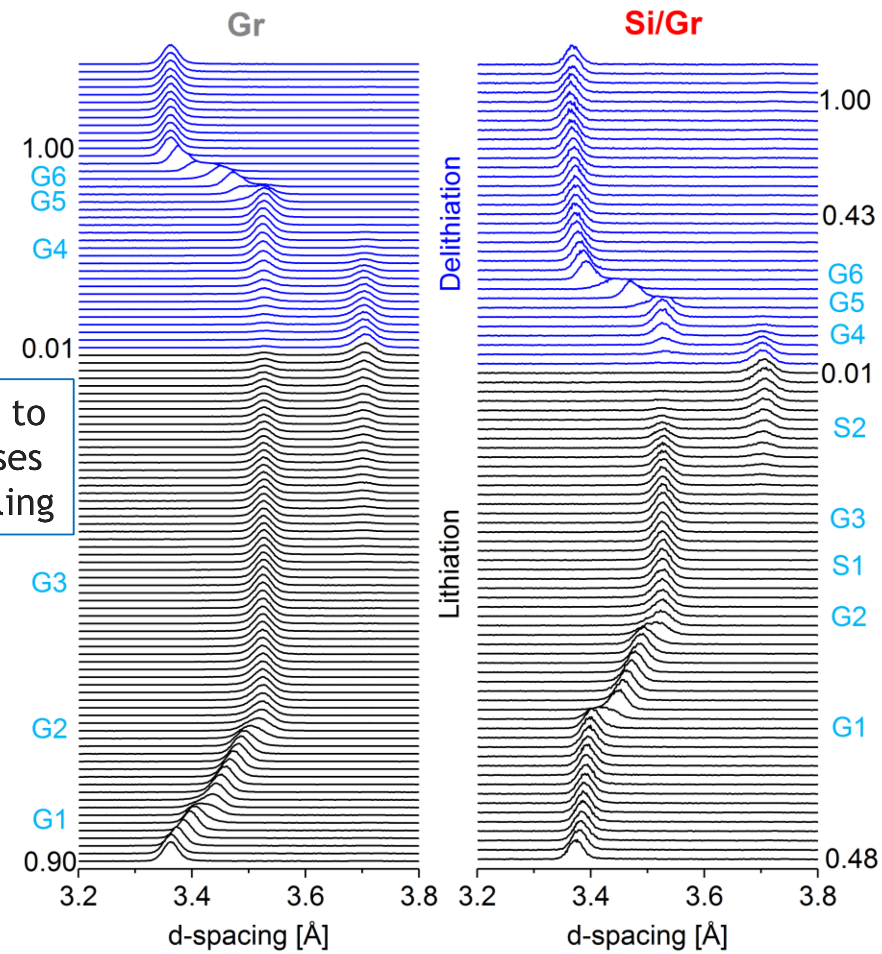
Graphite (002) peak evolution monitored using operando EDXRD. The Li_xSi species are X-ray amorphous (no peaks seen)



S3 plateau in Si-Gr results from delithiation of $Li_{15}Si_4$

Peak fitting done to identify Li_xC phases that form on cycling

Staging seen in Graphite. For Si-Gr Li^+ ion insertion occurs at higher voltages. Si component increases electrode capacity. S2 feature results from $Li_{15}Si_4$ formation.



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RELATIVE LITHIATION OF Si AND GRAPHITE IN Si/GRAPHITE (15/73 w/w) ELECTRODES

Capacity of the Si component inferred from the graphite capacity and cell-capacity data

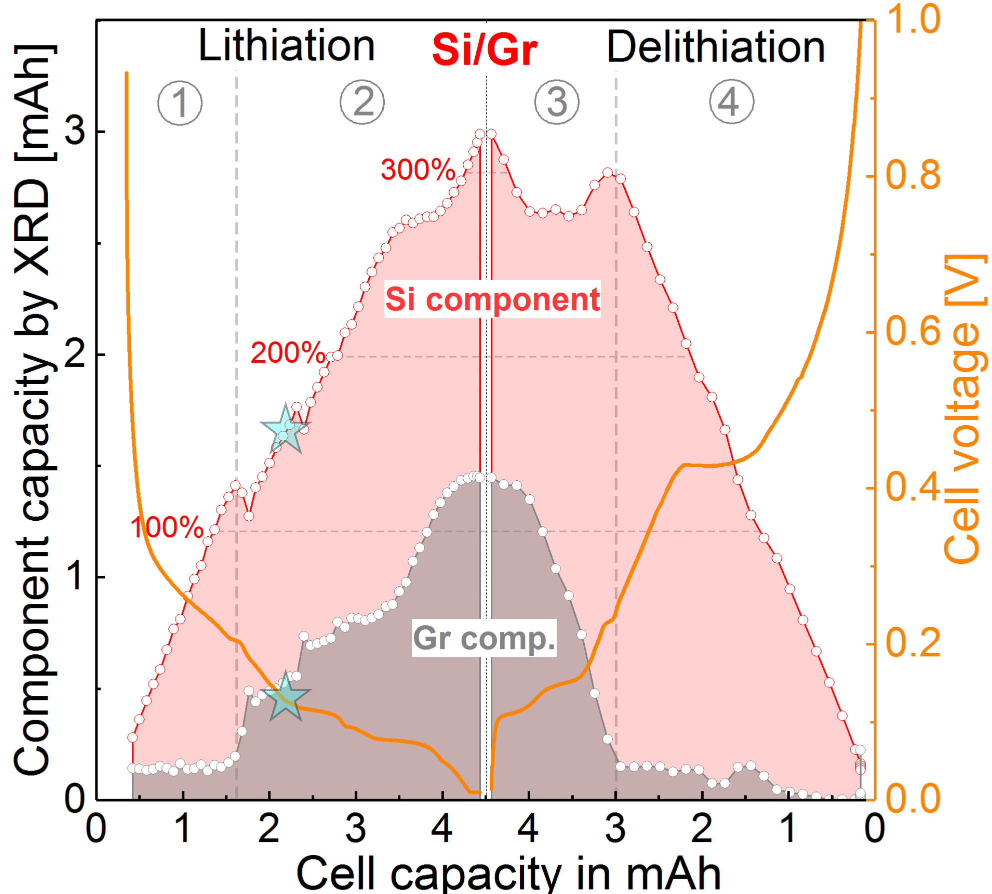
Region 1:
0.04 Li^+ in Gr per Li inserted
0.96 Li^+ in Si per Li inserted

Region 2:
0.42 Li^+ in Gr per Li inserted
0.58 Li^+ in Si per Li inserted

Region 3:
1 Li^+ in Gr per Li extracted
~0 Li^+ in Si per Li extracted

Region 4:
0.03 Li^+ in Gr per Li extracted
0.97 Li^+ in Si per Li extracted

Margin of uncertainty ~10%



☆ = negative potential is 0.14V; 180% Si expansion

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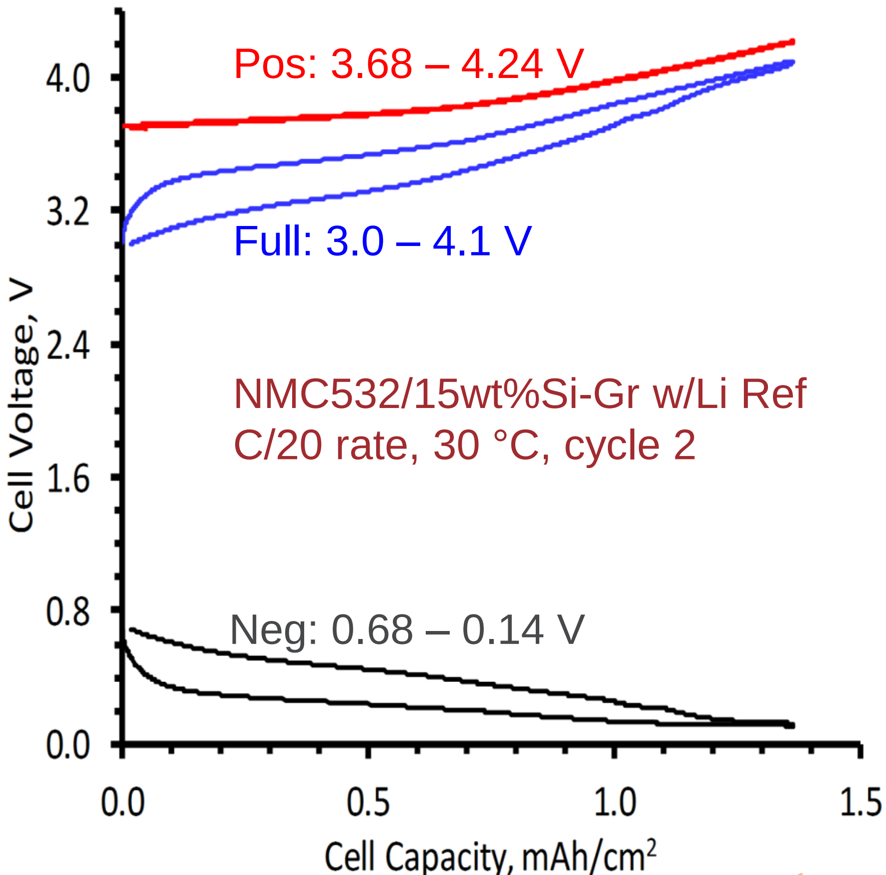
IS CAPACITY FADE OF Si-ELECTRODES SOLELY FROM VOLUME CHANGES?

Does the SEI formed on the Li_xSi compounds during Si-lithiation prevent reactions with the electrolyte?



Cycle-Life vs. Calendar-Life

During Cycle Life Aging

- Expansion/contraction of the silicon particles during lithiation/delithiation causes SEI to crack/flake off creating additional surfaces that reduce the electrolyte & trap Li^+ ions in the SEI causing capacity fade
- SEI residue clogs electrode pores and could cause particle isolation

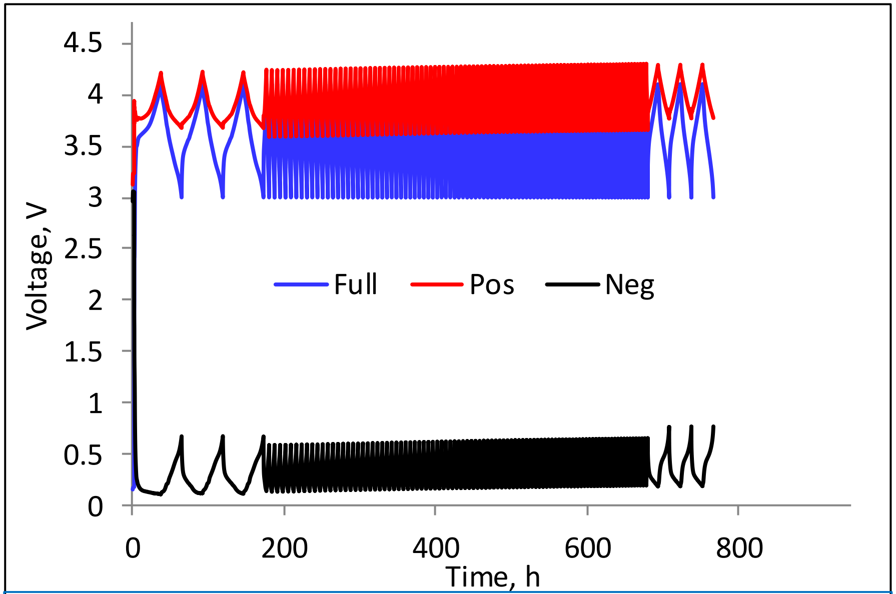
During Calendar Life Aging

- Silicon particles are at a fixed level of lithiation and hence at a fixed volume
- Thus, if the Li_xSi compounds forms a <u>truly passivating</u> SEI, cell capacity fade should be zero. If the capacity loss is not zero then the SEI is not fully passivating.

COMPARING CYCLE LIFE AND CALENDAR LIFE AGING: NMC532/GEN2-10%FEC/15%Si-GR

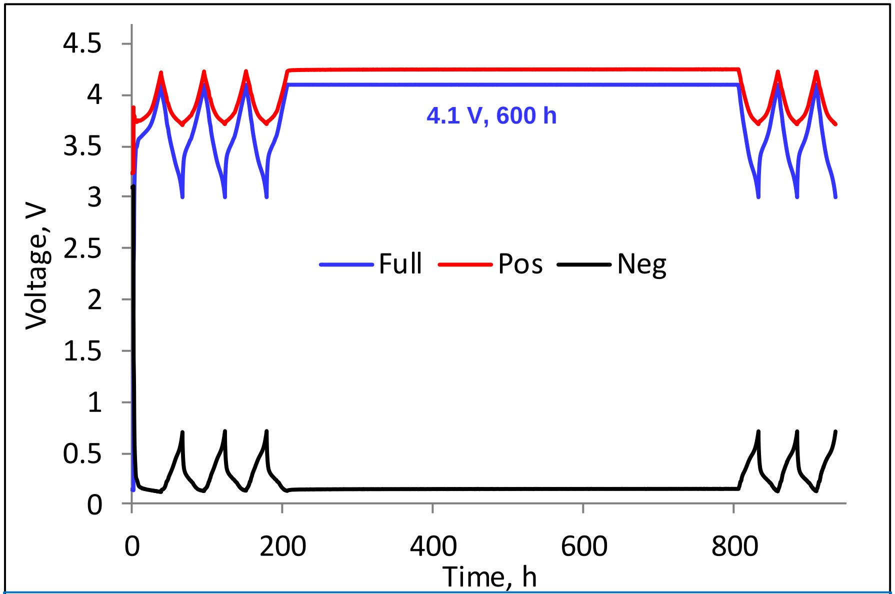
Cells contain a Li-metal reference electrode to determine electrode potentials during the aging tests (at 30 °C)

3.0-4.1 V, 3x C/20, 94x C/3, 3x C/20



The cell showed 44% capacity loss during the test. The loss is a consequence of volume changes in the Si particles that occur during cycling, which causes deterioration of the SEI; subsequent electrolyte reduction reactions trap mobile Li^+ ions causing capacity fade.

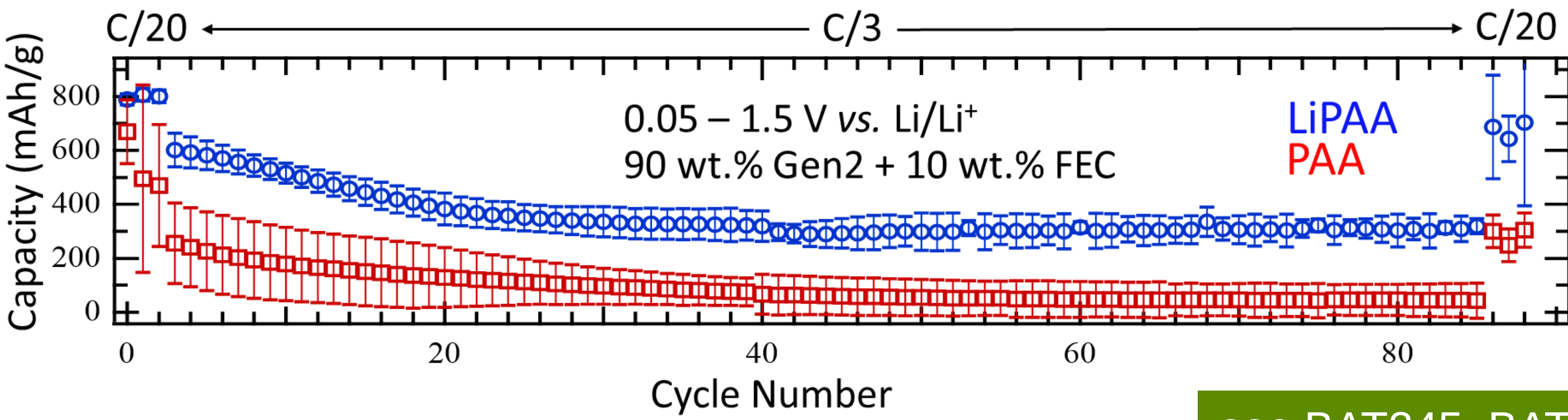
3.0-4.1 V, 3x C/20, 600 h hold at 4.1 V, 3x C/20



The cell showed ~3% capacity loss during the 4.1 V hold. Because Si-particle volume changes are not expected during this potential hold, the capacity loss can be attributed to slow (but continuing) electrolyte reduction reactions that immobilize Li^+ ions in the SEI.

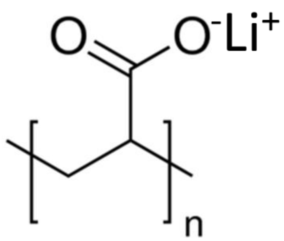
COMPETING FACTORS IMPACT PERFORMANCE OF SILICON ANODES MADE WITH DIFFERENT BINDERS

Overall, 15wt%Si-Gr composites processed with LiPAA binder in H_2O outperform those made with PAA binder in NMP solvent



see BAT345, BAT349

LiPAA/H_2O

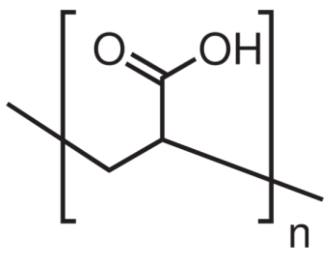


Lower water content in the electrode

Higher Coulombic efficiency

Less impedance rise

PAA/NMP



Less Si corrosion

Better adhesion to copper current collector

Better electrode uniformity

Hays, K. A. et al. *J. Power Sources* **2018,** *384*, 136-144.

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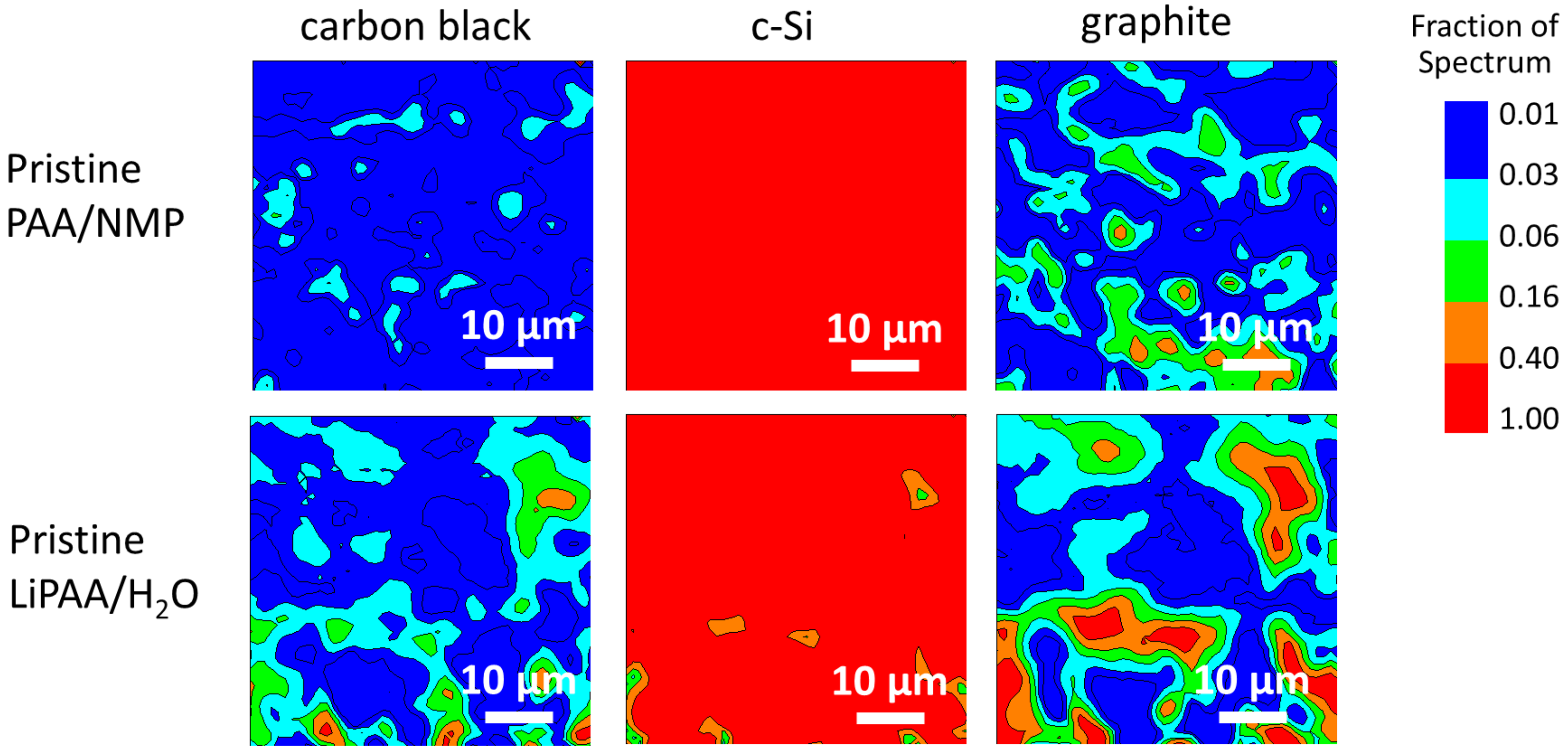
CHOICE OF BINDER AND SOLVENT SYSTEM IMPACTS ELECTRODE UNIFORMITY

Si-Gr composites processed with PAA binder in NMP have a more uniform distribution of active and inactive materials than anodes made with LiPAA binder in H_2O



Ruther, R.E. et al. unpublished 2018

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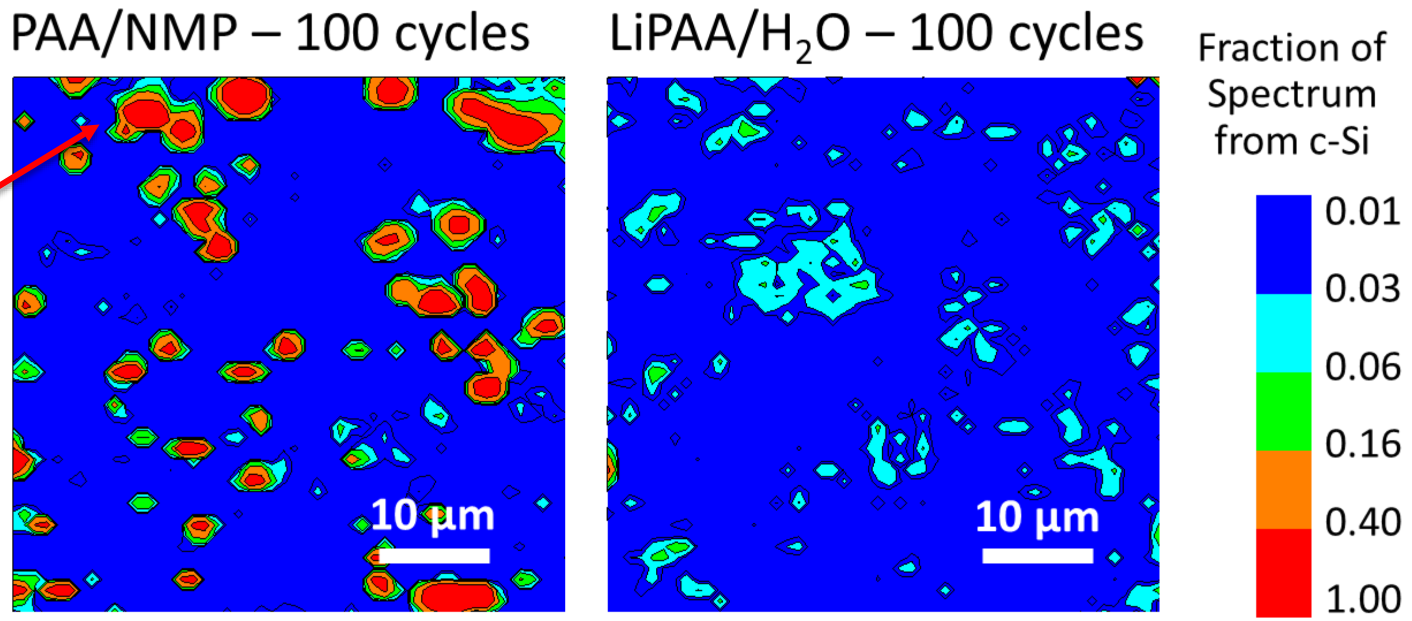
BINDER SELECTION IMPACTS SILICON UTILIZATION OVER LONG-TERM CYCLING.

PAA binder yields composites with more inactive silicon than LiPAA binder after 100 cycles.

Region with electro-chemically inactive c-Si



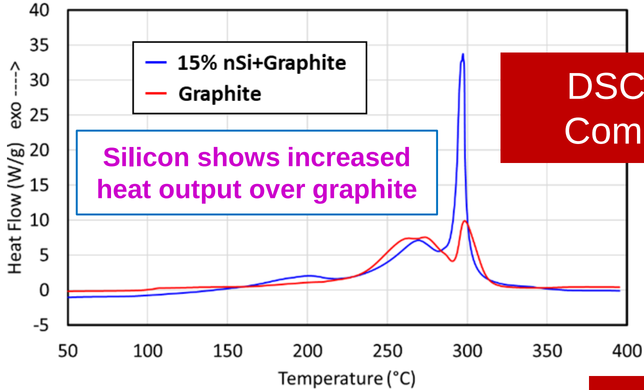
Better ionic and electronic connectivity contribute to better long-term performance with LiPAA-based anodes.

Ruther, R.E. et al. unpublished 2018

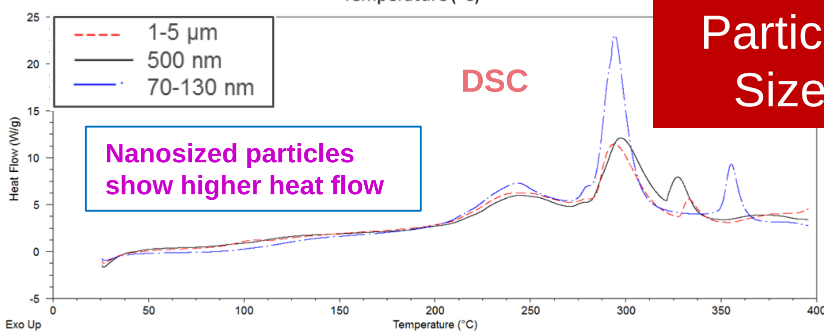
CALORIMETRIC ELECTRODE CHARACTERIZATION

Heat generation and peak heat flow trends with various parameters

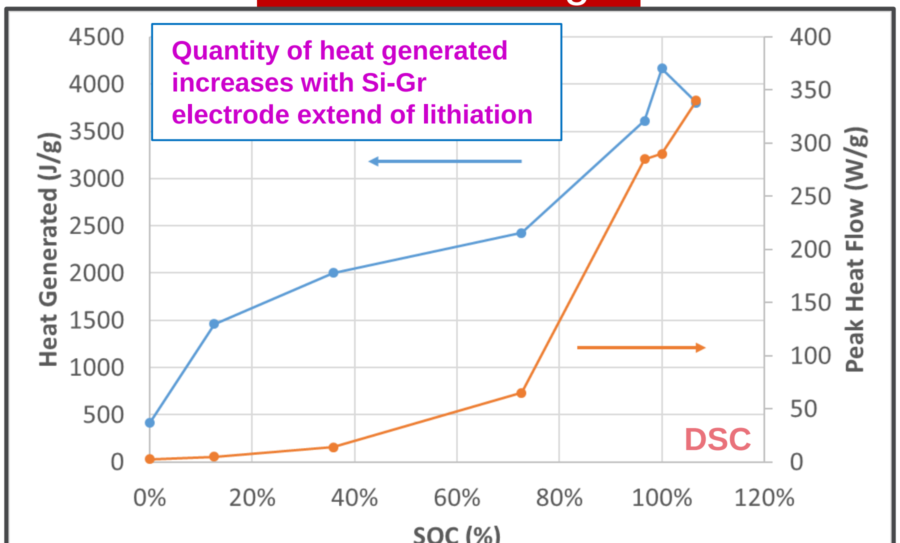
DSC Anode Comparison



Particle Size



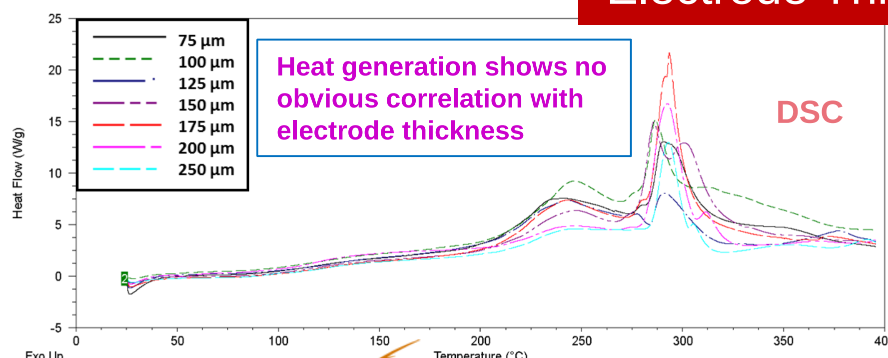
State of Charge

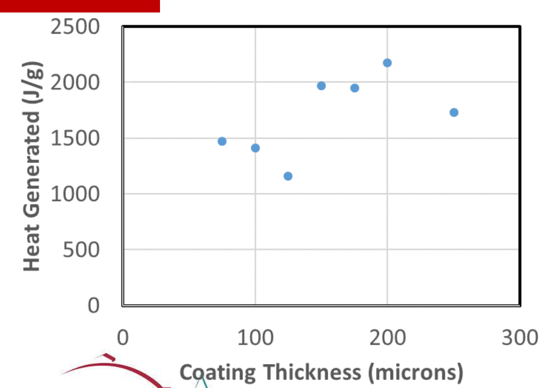


15%Si-Gr, Gen2 electrolyte, 5 cycles, 1.5-0.05 V vs. Li

Electrode Thickness

70-130nm NanoAmor silicon vs. Li
46 % coating porosity
15% nSi
73% MAG-E
2 % Timcal C45
10 % LiPAA





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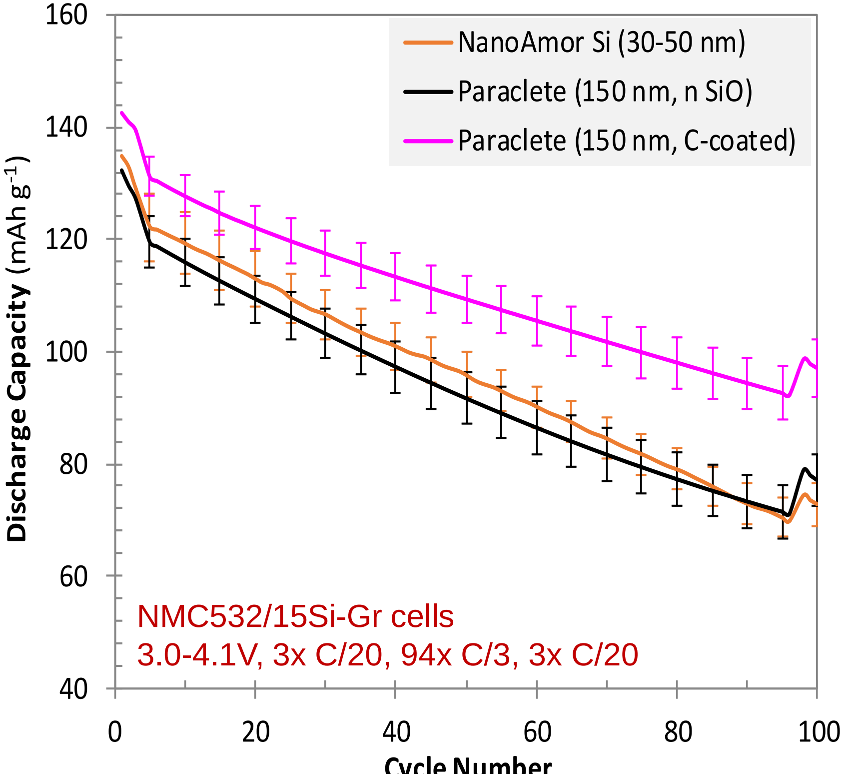
CARBON COATINGS ON SI PARTICLES CAN IMPROVE PERFORMANCE AND EXTEND CELL LIFE

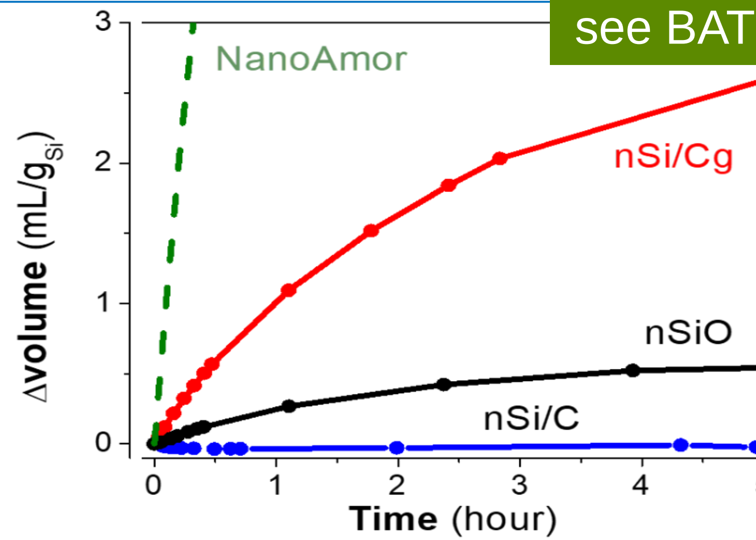
Improvements observed both in half- and full-cell configurations



Capacity retention of cells with the C-coated Si particles is ~70%, with the oxidized silicon (nSiO) is 58%, and with the NanoAmor Si is 54%

An added benefit of the carbon coating is that it reduces gas (H_2) evolution during electrode fabrication from aqueous slurries.

see BAT345



Gas evolution (determined by Archimedes method) from aqueous slurries containing LiPAA and Si particles (from Paraclete) with graphene-coating (nSi/Cg), oxidized-surface (nSiO) and C-coating (nSi/C). Data for NanoAmor Si are also shown.

SUMMARY

- Operando EDXRD can be used to track the lithiation state of Graphite and Silicon in Si-Gr electrodes
  - The Gr-lithiation state can be tracked directly and the Si-lithiation state can be inferred from the cell capacity data.
- Capacity loss during cycle-life tests is greater than the capacity loss during calendar-life tests
  - Volume changes in Si-particles are the primary trigger for capacity loss. However, the loss measured during the calendar-life potential hold indicates that electrolyte reduction reactions continue on the lithiated Si-particles.
- Si-Gr composites made with LiPAA binder outperform anodes with PAA binder
  - Performance differences are not explained by electrode uniformity and first-cycle electrochemical activity. Fundamental interactions at the polymer/silicon and polymer/graphite interface should be explored.
- Carbon coatings on Si nanoparticles extends life during electrochemical cycling
  - The carbon coatings (and thick oxide layers) can also reduce H_2 evolution during electrode fabrication from aqueous slurries
- Cells containing silicon shows an increase of gas and heat generation during abuse testing relative to a graphite only cell
  - State of charge and silicon particle size influence the extent of the response, while the electrode thickness appears to have a minimal impact

FUTURE WORK

- Operando experiments will be conducted to determine the relative lithiation of active components in electrodes containing various Si contents (5, 10, 70 wt%)
  - Volume changes of the Si component will be correlated with volume changes of the electrode during cycling
- Lithium-ion cell chemistries, which are suitable for cycle-life aging may not be optimal during calendar-life aging.
  - Experiments will be conducted to optimize the electrolyte chemistry and electrode compositions

see BAT352

- Characterize inhomogeneity in lithium transport and SOC variation using *in situ* and *ex situ* Raman mapping along the thickness of Si-Gr and NMC electrodes
  - Study SEI formation and electrode degradation *in operando* with acoustic time-of-flight (TOF) measurements (with Dan Steingart, Princeton)
- Investigate contributions of silicon properties and electrode/electrolyte interfacial properties to overall gas generation during thermal/overcharge abuse conditions.
  - Focus will be on minimization of energy release and gas generation without compromising electrochemical performance and cell life

see BAT349

Any proposed future work is subject to change based on funding levels.

RESPONSES TO PREVIOUS YEAR REVIEWERS' COMMENTS

Last year two poster presentations covered all the project. The two posters were each reviewed by eight reviewers. We thank the reviewers for their thoughtful comments. Selected excerpts are given below.

- Many of the reviewers' comments were generally positive.
  - "applauded the excellent, thorough approach"
  - "very ambitious program to assess advantages, disadvantages and solutions for Si anode materials"
  - "very nice intra-laboratory coordination"
- One reviewer thought we could further enhance the program by bringing in experts in mechanical stresses. We conduct limited mechanical measurements and have relied on literature to establish a stable particle size, but in general we agree more in-depth studies could improve the program.
- One reviewer suggested that our commitment to openness limits our ability to examine proprietary materials. We agree totally and recognize the limitation. However, we consider that the work we are doing is addressing the fundamental issues with silicon materials and will benefit the entire community.

REMAINING CHALLENGES AND BARRIERS

- Several key challenges remain that limit integration of silicon into graphitic negative electrodes, mostly related to the large crystallographic expansion of silicon (>300%) upon lithiation.
  - SEI stability issues, which affect cycling efficiency.
  - Electrode stability issues that include particle isolation, accommodating volume changes, and adherence.

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

- Six National Laboratories have teamed to form this integrated effort focused on gaining insights into and advancement of silicon-based materials, electrodes, and cells.
- This effort has strong interactions with the Silicon Electrolyte Interface Stabilization (SEI-Sta) project (BAT344, BAT345, BAT346, BAT347, and BAT348).
- Paraclete Energy is suppling baseline silicon materials.

CONTRIBUTORS AND ACKNOWLEDGMENT

Research Facilities

- Post-Test Facility (PTF)
- Materials Engineering Research Facility (MERF)
- Cell Analysis, Modeling, and Prototyping (CAMP)
- Battery Manufacturing Facility (BMF)
- Battery Abuse Testing Laboratory (BATLab)

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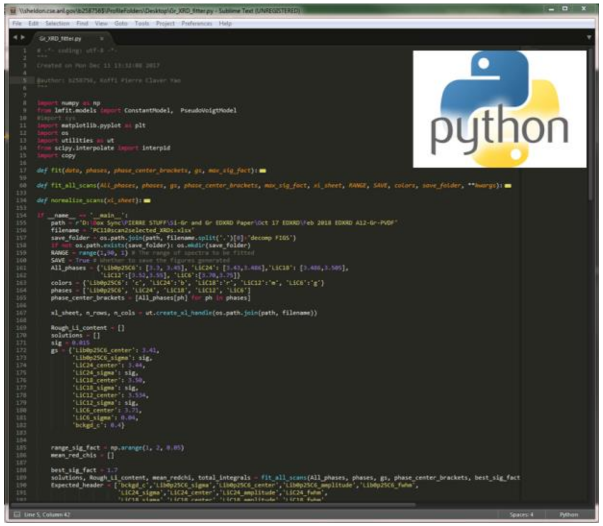
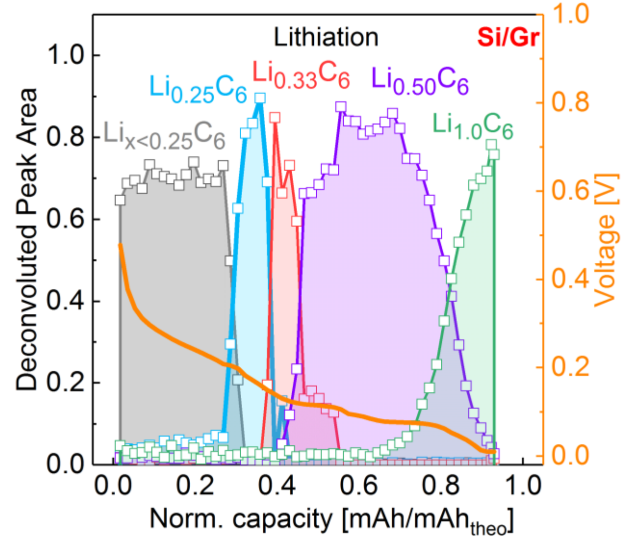
TECHNICAL BACKUP SLIDES

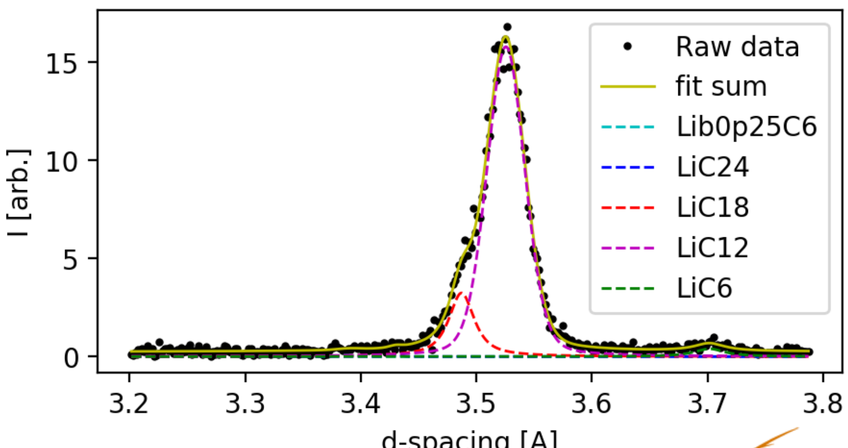
DECONVOLUTION OF GRAPHITE STAGING FOR QUANTIFICATION OF FRACTIONAL LITHIATION IN SI/GR BLENDED ANODE ELECTRODES



Custom code necessary to quantify Lithium-Graphite (Li-Gr) intercalation compounds in Silicon-Graphite blended electrodes

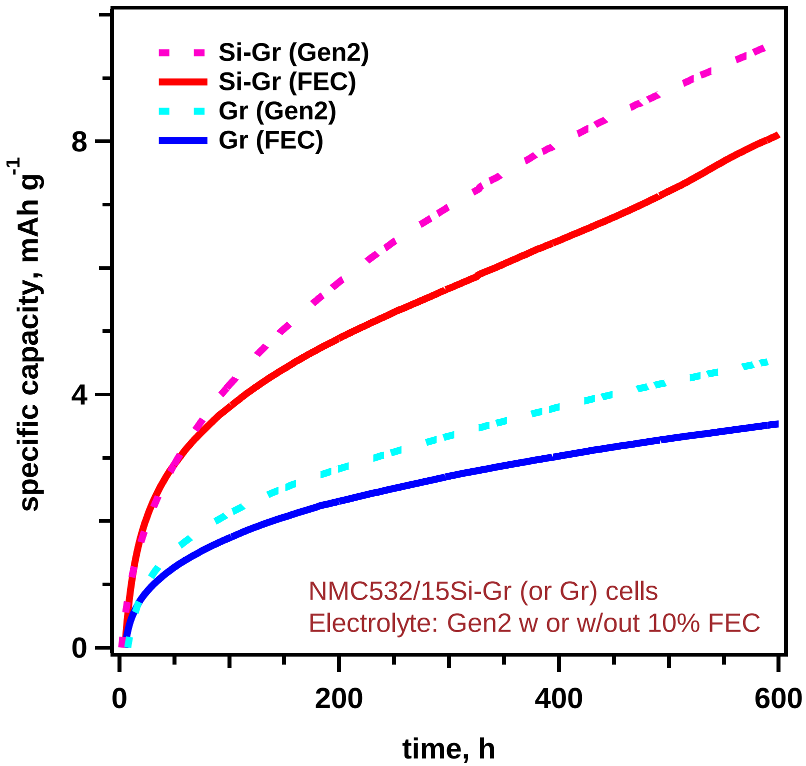


Quantification of Li-Gr phases as a function of state of charge in a Si/Gr blended electrode in the form of the integral of the deconvoluted peaks.



Example of deconvolution of Li-Gr phases

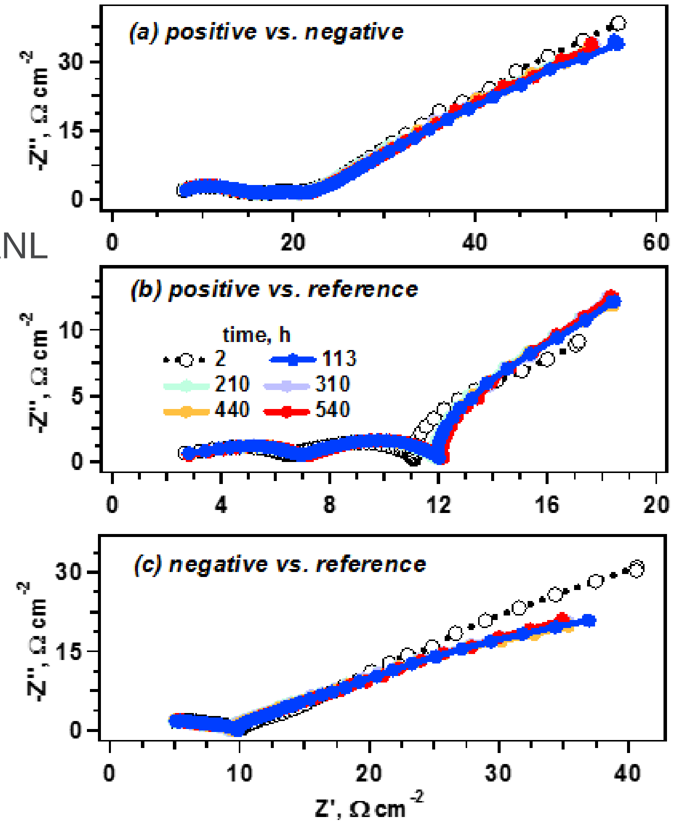
CALENDAR LIFE AGING: CAPACITY FROM PARASITIC CURRENTS DURING POTENTIAL HOLD (600 h, 4.1 V)



Capacity change during potential hold is greater for cells with Si-Gr electrodes than Gr electrodes. Also cells with FEC show smaller capacity changes indicating that the FEC helps form a better (but not perfect) passivation layer.

EIS data (100 kHz – 0.01 Hz, 30 °C) show that the full cell and electrode impedances are barely altered during the potential hold

K. Kalaga, ANL



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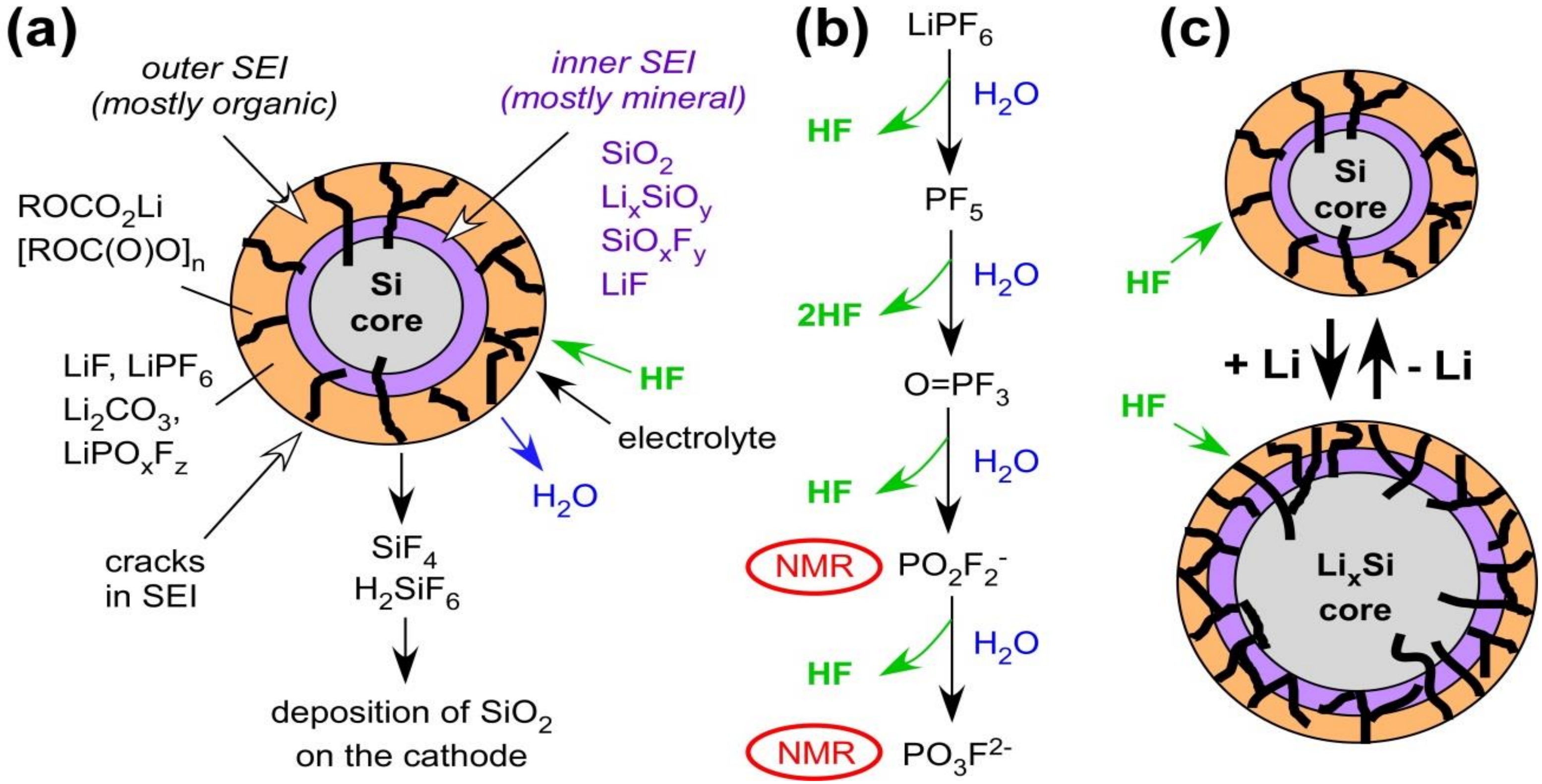
ADVANCED STAGE OF CYCLE-LIFE AGING – SCHEMATIC REPRESENTATION OF MECHANISMS

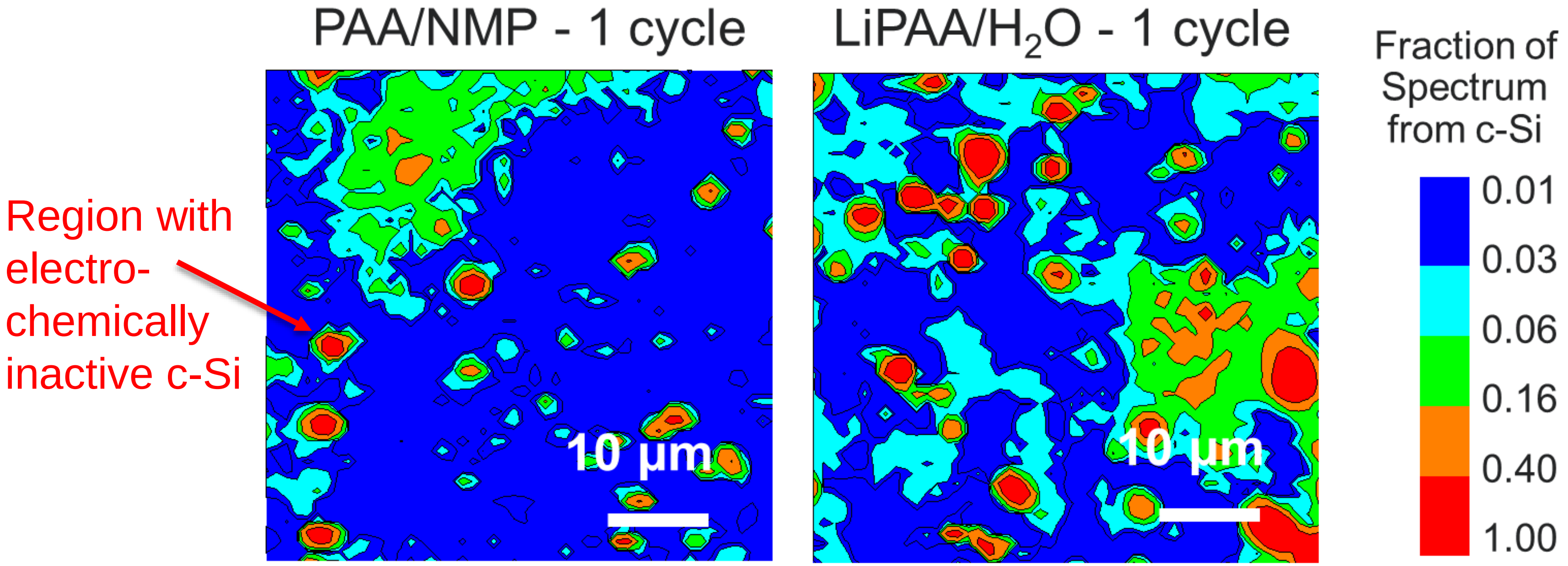


- Electrolyte and HF diffuse through pores and cracks in the outer SEI and react with the particle interior, releasing SiF_4 and water molecules back into the electrolyte. This water joins the hydrolytic cycle for $LiPF_6$ (shown in panel b).
- As Si particles repeatedly expand and contract, deep cracks develop allowing access of HF to the core, resulting in its digestion and additional SEI formation.

INITIAL SILICON LITHIATION IS LARGELY INDEPENDENT OF BINDER

R. Ruther, ORNL

Domains of electrochemically inactive silicon are similar in size and extent with both PAA and LiPAA binders.



Raman spectroscopy data does not explain the differences in electrochemical performance between the binder systems. Other fundamental factors (polymer/surface interactions, SEI chemistry) may explain the better long-term performance of LiPAA-based Si-Gr composites and merit further study.

Ruther, R.E. et al. unpublished 2018